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10/518695

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IN THE SPECIFICATION:

Page 1, delete the whole paragraph starting in line 1 and replace it with the following new paragraph:

The invention relates to a method according to the preamble of claim 1 for depositing a layer on a substrate.

Page 1, delete the whole paragraph starting in line 3 and replace it with the following new paragraph:

The invention also relates to an apparatus according to the preamble of claim-34 for depositing a layer on a substrate.

Page 7, delete the whole paragraph starting in line 13 and replace it with the following new paragraph:

In the International patent application-WO 01/96234 A2 U.S. Patent 6,635,191 it has been proposed to apply catalytically active layer to metallic substrates by sputtering. To accomplish a proper adhesion, the starting material is an alloy containing iron, chromium, aluminum and yttrium. Beforehand, these alloys are heated in air at 1100°C for 50 hours. This leads to formation of aluminum oxide or chromium oxide crystallites on the alloy surface. Thereafter, the thus pretreated alloy surface is covered with a layer of metallic magnesium and nickel. This is done by sputtering, whereby the metal is atomized by argon ions incident on that metal, which ions have been formed in a glow discharge in argon of a low pressure.

Page 7, delete the whole paragraph starting in line 23 and replace it with the following new paragraph:

According to the method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191, magnesium and nickel are atomized simultaneously. To obtain a uniform composition, the metal surface to be covered is spun at 10 rpm. Evidently, this is possible only with relatively small substrates. The method described in the International patent application WO 01/96234 A2 U.S. Patent 6,635,191 covers perforated alloy discs of a

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diameter of only 13 mm. For covering larger metal or alloy surfaces, the method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191 is therefore less suitable.

Page 8, delete the whole paragraph starting in line 1 and replace it with the following new paragraph:

The method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191 leads to the application of a layer of metallic nickel and magnesium atoms to the surface of the thermally pretreated alloy. Such a layer is not suitable as a catalyst, since the porosity of the layer is very low and hence the exposed catalytically active surface is also small. When a second catalytically active component is applied to the nickel-magnesium layer, such as the rhodium that is applied in a second preparation step according to the method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191, this second component will not expose any large surface either. Therefore, according to the method of the International patent application WO 01/96234 A2, U.S. Patent 6,635,191 the magnesium and nickel are oxidized by heating the covered alloy surface in air or oxygen. Heating is done at temperatures of from 800 to 1000 °C and preferably at 900 °C. Heating is done for 2 to 6 hours, preferably for 4 hours.

Page 8, delete the whole paragraph starting in line 1 and replace it with the following new paragraph:

It will be clear that the adhesion of the nickel and magnesium containing layer is adversely affected by the oxidation. As a result of the oxidation, the volume of the layer increases, so that the layer applied is subject to tension. Also, the porosity of such a layer will be low. For that reason, to raise the porosity of the layer, according to the method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191, the nickel oxide in the layer is reduced by heating in a hydrogen containing stream at 900 °C for 4 hours. In that case, the nickel oxide alone is reduced, while the magnesium oxide does not react. According to the method of International patent application WO 01/96234 A2 U.S. Patent 6,635,191, the catalytically most active component, the rhodium, is then applied, by sputtering, onto the layer obtained after reduction of the nickel oxide. It will be clear that in this way the

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catalytically most active component cannot be provided deeply into the pores of the porous layer obtained by reduction of the nickel oxide-magnesium oxide.

Page 9, delete the whole paragraph starting in line 1 and replace it with the following new paragraph:

The method according to the International patent application WO 01/196234 A2 accordingly U.S. Patent 6,635,191 has the following drawbacks. The desired configuration of a catalytically active component on a porous carrier can only be effected by first oxidizing the primarily applied mixture of a base and a less base metal and then reducing the less base metal oxide. It is clear that in this way the porous structure of the layer as applied cannot be properly set. Also, the distribution of a catalytically more active component to be subsequently applied is difficult to control according to the method of the International patent application WO 01/96234 A2 U.S. Patent 6,635,191. In addition, with this method, it is not possible to manufacture catalysts according to an in-line process. Therefore, this method is comparatively little attractive from a commercial viewpoint. Moreover, during the manufacture of catalysts according to this method, a relatively large part of the catalyst material is lost in that only a small part of the material in effect contacts the substrates and subsequently remains behind on the substrate. Therefore the known method is costly and environmentally harmful.

Page 9, delete the whole paragraph starting in line 26 and replace it with the following new paragraph:

Contrary to the patent application of Hoechst A.G. discussed above, EP 1034 834 of Sulzer Metco A.G. particularly aims at the application of catalytically active layers on metallic surfaces. To cover a large surface, the plasma is generated at low pressure. Moreover, to increase the surface covered, the plasma source is swiveled. Although a large surface can be covered in this manner, the density of the plasma is such that only very thin layers can be applied. In the method according to the patent application EP 1034 643 of Sulzer Metco A.G., a uniform gas pressure of 15 to 1500 Pa is used, and preferably a pressure of 100 to 600 Pa. In the method according to the <u>Dutch</u> patent application no.1020923 of O.T.B., upon which this application relies for priority under 35 U.S.C. §119, a pressure lower

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than 50 mbar $(5x10^4 \text{ Pa})$ and preferably lower than 5 mbar. $(5x10^3 \text{ Pa})$ is used in the processing chamber, as stated in column 1, lines 46 to 48. The gas pressure according to the method of Sulzer Metco A.G. is so low, that it only results in a low deposition rate. As is reported in column 2, lines 23 to 25, such low gas pressures result in plasma flames with a length of, for instance, 2.5 m.

Page 11, delete the whole paragraph starting in line 19 and replace it with the following new paragraph:

In the method according to the PCT application WO 01/32949 U.S. Patent 6,800,336of Agrodyn Hochspannungetechnik GmbH and Fraunhofer-Gesellschaft zur Forderung der angewandten Forschung, a plasma arc generated using an AC voltage is used. The applicants consider the introduction of the substrate into an evacuated processing chamber difficult to carry out in a continuous manner and therefore have as their object to describe a process which can be carried out at atmospheric pressure. In the application, it is stated that it is part of the state of the art to generate a plasma by letting a corona discharge take place at atmospheric pressure. It is also part of the state of the art to introduce into the plasma a gaseous precursor of the material to be applied and to realize deposition of the desired material in this manner. In this manner, however, only deposition rates of 10 to 20 µm per second (page 1, line 32) are achieved. Furthermore, the plasma is only formed in a small zone between the source and the workpiece, enabling one to operate only when the distances between the plasma source and the workpiece are short. According to this known method, the corona discharge generating the plasma is not to take place in a stationary gas atmosphere, but in a gas flow. The plasma flow thus obtained is directed to the surface to be covered, so the counter electrode no longer needs to be provided below the substrate (page 2, lines 20 to 22). A gaseous precursor of the material to be applied is supplied into the plasma flow relatively close to the surface to be covered. In this manner, premature emptying of the precursor is prevented (page 2, lines 22 to 31).

Page 12, delete the whole paragraph starting in line 13 and replace it with the following new paragraph:

A drawback of the method according to the PCT application WO 01/132949 U.S.

Patent 6,800,336 of Agrodyn Hochspannungstechnik GmbH aril Fraunhofer Gesellschaft zur

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Förderung der angewandten Forschung is the small surface covered by the plasma beam.

Also, of by no means all carrier materials and catalytically active materials gaseous compounds having a sufficiently high vapor pressure are available. The applicants are of the opinion that solid particles can also be supplied to the plasma flow; according to lines 21 to 24 of page 8, solid substances or liquids can be supplied to the plasma flow, which sublimate or vaporize in the plasma flow. However, [[for,]] for instance, carrier materials such as aluminum oxide and zirconium dioxide, sublimating or vaporizing is very difficult to realize. Moreover, according to the method of WO 01/132949 U.S. Patent 6,800,336, an AC voltage is used to generate the plasma flow. The atmospheric pressure at which the process is carried out and the AC voltage source form a clear distinction from the method according to the invention to be described hereinafter.

Page 13, delete the whole paragraph starting in line 7 and replace it with the following new paragraph:

The object An aspect of the present invention is to eliminate the disadvantages of the known methods while maintaining the advantages thereof. In particular, the invention contemplates a method of applying preferably porous, properly bonding catalyst layers of a uniform, properly settable chemical composition, to substrates.

Page 13, delete the whole paragraph starting in line 12 and ending in line 13.

Page 18, delete the whole paragraph starting in line 1 and replace it with the following new paragraph:

The invention further relates to an apparatus <u>in</u> which is characterized by the features of claim 84. With this apparatus, catalysts can be produced relatively fast and with a high uniformity over a large surface. The use of the plasma cascade source then offers the abovementioned advantages.

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Page 18, delete the whole paragraph starting in line 21 and replace it with the following new paragraph:

As shown in Fig. 2, the plasma cascade source 3 is provided with a cathode 10 that is present in a source chamber 11 and an anode 12 that is present at a side of the source 3 proximal to the processing chamber 2. Via a relatively narrow channel 13 and the plasma outlet opening 4, the source chamber 11 opens into the processing chamber 2. The apparatus is dimensioned such that the distance L between the substrate 1 and the plasma outlet opening 4 is approximately 200 mm - 300 mm. In this manner, the apparatus can have a relatively compact design. The channel 13 is bounded by the mutually electrically insulated cascade plates 14 and the anode 12. During the treatment of a substrate, the processing chamber 2 is maintained at a relatively low pressure, in particular lower than 60 mbar, and preferably lower than 5 mbar. Naturally, inter alia the treatment pressure and the dimensions of the processing chamber should be such that deposition can still take place. In practice, the treatment pressure for a processing chamber of the present exemplary embodiment has been found to be at least approximately 0.1 mbar for this purpose. The pumping means pump needed to obtain the treatment pressure are not shown in the drawing. Between the cathode 10 and anode 12 of the source 3, a plasma is generated, for instance by ignition of an inert gas, such as argon, which is present therebetween. When the plasma has been generated in the source 3, the pressure in the source chamber 11 is higher than the pressure in the processing chamber 2. This pressure can be, for instance, substantially atmospheric and be in the range of 0.5-1.5 bar. Because the pressure in the processing chamber 2 is considerably lower than the pressure in the source chamber 11, a part of the generated plasma P expands such that it extends through a relatively narrow channel 7, from the outlet opening 4, into the processing chamber 2 to make contact with the surface of the substrate 1.